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Eco-Technological Process of Glass-Ceramic Production From Galvanic Sludge and Aluminium Slag

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Abstract:

Methods of purification of waste water which are most commonly used in the Republic of Serbia belong to the type of conventional systems for purification such as chemical oxidation and reduction, neutralization, sedimentation, coagulation, and flocculation. Consequently, these methods generate waste sludge which, unless adequately stabilized, represents hazardous matter. The aluminium slag generated by melting or die-casting aluminium and its alloys is also hazardous matter. In this sense, this paper establishes ecological risk of galvanic waste sludge and aluminium slag and then describes the process of stabilization of these waste materials by means of transformation into a glass-ceramic structure through sintering. The obtained product was analyzed with Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD). The object of the paper is the eco-technological process of producing glass-ceramics from galvanic sludge and aluminium slag. The aim of the paper is to incorporate toxic metals from galvanic sludge and aluminium slag into the glass-ceramic product, in the form of solid solutions.

Keywords: Galvanic sludge, Aluminium slag, Glass-ceramics, Ecological risk.

Introduction

Galvanic processing of metal and secondary processing of aluminium generate waste with high concentration of toxic metals.

In open space, galvanic sludge reacts with atmospheric precipitation with low pH value initiating highly toxic and chemically active ions and metals, given in the following chemical equations:



where: Me=Cu, Zn, Cd, Ni, Pb, etc.

Heavy metals are non-biodegradable and accumulate permanently in the environment, which is how they enter the food chain and indirectly affect human life and health.

Aluminium slag is very heterogeneous and thermodynamically and chemically unstable. Inside molten slag there is a possibility of numerous double exchange reactions, reactions typical for glasses, interaction between metal oxides and chlorides of the following type:



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These processes usually yield evaporable and hygroscopic products. After the removal and disposal of aluminium slag, mostly in open space, many processes occur, connected with crystallization of particular slag components, with solidification of amorphous slag components, and with the process of hydrolysis of numerous chlorides and fluorides.

Integral environmental protection requires that such waste should be stabilized prior to final disposal.

Stabilization of toxic metals from such waste is performed with various techniques, such as sintering [1, 2], transforming sewage sludge and galvanic sludge into glass-ceramics [3], obtainment and properties of glasses and glass-ceramics from coal fly ash [4], vitrification [5], solidification of galvanic sludge by asphalt emulsions [6], and others.

Thus, chemically active substances (Cu^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) are transformed, by phase and chemical transformations, into a stable structure, where pollutants cannot be set off even in critical conditions such as high temperature, acidic or basic influence, etc.

Experimental

Ecological risk

Ecological risk of waste sludge and aluminium slag is determined on the basis of defining high-flow and low-flow fractions of a series of metals by a standard procedure U.S.EPA 1997/222. The primary ecological risk of waste sludge was determined on the basis of rinsing representative samples in distilled water and analyzing metal with atomic absorption spectrophotometry (*Perkin Elmer AAM1100 and Varian AA-20*). In the results the term water eluate has been adopted for this movable fraction.

For the sake of a more detailed insight into the pollution potential, and at the same time bearing in mind the chemical origin of waste sludge and aluminium slag, a low-flow fraction was also determined, which is more strongly bonded and thus represents a pollutant reservoir. A low-flow metal fraction was also isolated by a standardized procedure of rinsing with diluted nitric acid. This fraction is marked as HNO_3 -eluate. The criteria based on which the comparison of concentration of metals in water after rinsing the representative samples of waste sludge was carried out are taken from the Holland list 8935/1998.

The results are shown in Tab.s I and II where A is the referential value for standard groundwater and B is the concentration at which detailed testing and safety measures are recommended (EEC regulation) [7].

Tab. I Comparison of concentrations of high-flow (H_2O -eluate) and low-flow (HNO_3 -eluate) metal fractions in representative samples of waste sludge

Pollutant	H_2O -eluate (mg/l)	HNO_3 -eluate (mg/l)	A (mg/l)	B (mg/l)	Failure to meet criteria
Cu	0.137	106.1	0.015	0.050	A, B
Zn	0.269	1222	0.150	0.200	A, B
Cr	9.56	977	0.001	0.050	A, B
Ni	1.935	1210	0.015	0.050	A, B
Cd	2.839	1203	0.005	0.050	A, B
Pb	0.000	9.585	0.005	0.050	A, B

Tab. II Comparison of concentrations of high-flow (H₂O-eluate) and low-flow (HNO₃-eluate) metal fractions in representative samples of aluminium slag

Pollutant	H ₂ O-eluate (mg/l)	HNO ₃ -eluate (mg/l)	A (mg/l)	B (mg/l)	Failure to meet criteria
Cu	3.972	8.261	0.015	0.050	A, B
Zn	0.536	2.315	0.150	0.200	A, B
Cr	1.216	15.441	0.001	0.050	A, B
Mn	0.326	0.650	0.050	0.100	A, B
Be	0.7815	0.8069	0.0002	0.0005	A, B
Ti	0.533	2.287	0.100	0.150	A, B
Al	88.816	109.359	*	*	A, B

* The values for aluminium were not standardized under the A and B criteria.

The presented data indicate that the concentration of toxic metal after rinsing of composite samples of galvanic sludge and aluminium slag is higher than that in standard groundwater (criterion A). The Holland list 8935/1998 also recommends safety measures – purification of seepage water in case waste is disposed of unprocessed.

Eco-technological procedure of waste sludge treatment

The primary material used in the eco-technological process is galvanic sludge. Qualitatively, galvanic sludge consists of toxic metal hydroxides (Cu(OH)₂, Cr(OH)₃, Zn(OH)₂, Pb(OH)₂, Cd(OH)₂, Ni(OH)₂, and others).

The second material is waste aluminium slag, which contains certain amounts of aluminium, metal oxides (Al₂O₃, BeO, TiO₂, CuO, Cr₂O₃, and others), and predominantly Al₂O₃ and solidified refinement salts, which mostly contain KCl, NaCl, Na₃AlF₆, MgCl₂, CaF₂, MgF₂, etc.

Waste glass was used as an auxiliary material. Average composition of waste glass in mass percentage is 76% SiO₂, 11% PbO, 8% ZnO, 2% B₂O₃, 2% BaO, and 1% ZrO₂.

Apart from the basic waste materials, boron trioxide (B₂O₃) was also used as a liquefier for glass-ceramics synthesis.

Since aluminium slag contains high-flow fluorides which could destroy glass-ceramics phase, it is rinsed with water in order to remove the fluorides. The slag is sunk in the water and left like that for 24 hours, during which the fluorides dissolve. The insoluble part of the slag is separated by filtration and fluorides are regenerated by evaporation and crystallization. The residue thus obtained is then processed further.

To obtain dehydration, it is necessary to dry the galvanic sludge. A low-temperature dry kiln can be used for this purpose.

After these operations all the elements (sludge, slag, glass, and borax) are ground in a colloid mill to facilitate melting. When the ingredients are ground, they are mixed until the mixture is homogenized and then the same mixture is poured into the melting mould.

The mould with the mixture is put into a blast furnace where it is heated at 1200-1400°C. The melting temperature of the mixture depends on the quantity of several components included in the mixture. An increased quantity of glass will lower the melting temperature and reduce the solidity of the obtained ceramics. With the increase in the quantity of aluminium slag the solidity of the ceramic structure will also increase, but this requires a higher melting temperature, which sometimes presents a difficulty.

In order to get to phase transformations, the mixture has to be absolutely liquid, which is why the mould is kept in the blast furnace for about 40 minutes. After melting, the melted

content is poured into a preheated graphite mould. The preheated graphite mould is preheated at 250-300°C so that glass-ceramics would not crack due to sudden cooling in a cold mould.



Fig. 1. Glass-ceramic sample

The analyses of determining the concentration of metals in the obtained glass-ceramics show absence of metals in the water in which the sample is rinsed, which proves the efficiency of the method of stabilization of this waste.

Results and Discussion

The efficiency of the eco-technological procedure of transforming galvanic sludge and aluminium slag into a sTab. glass-ceramic structure was confirmed with Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD).

Infrared spectra of glass-ceramics were obtained with a BOMEM (Hartman & Braun) FT-IR spectrophotometer, model MB-Series, in a spectral range 4000 to 400cm⁻¹, with a resolution of 2cm⁻¹, by method of pressed pellets. The Potassium Bromide (KBr) Technique for sample preparation was used to record spectra. A quantity of 1-2 mg of tested sample is mixed with 150 mg of spectroscopically pure KBr. The mixture is then vacuumed and pressed at 200 Mpa, which forms thin permeable pellets. A reference pellet for BACKGROUND recording was prepared from pure KBr (fig. 2).

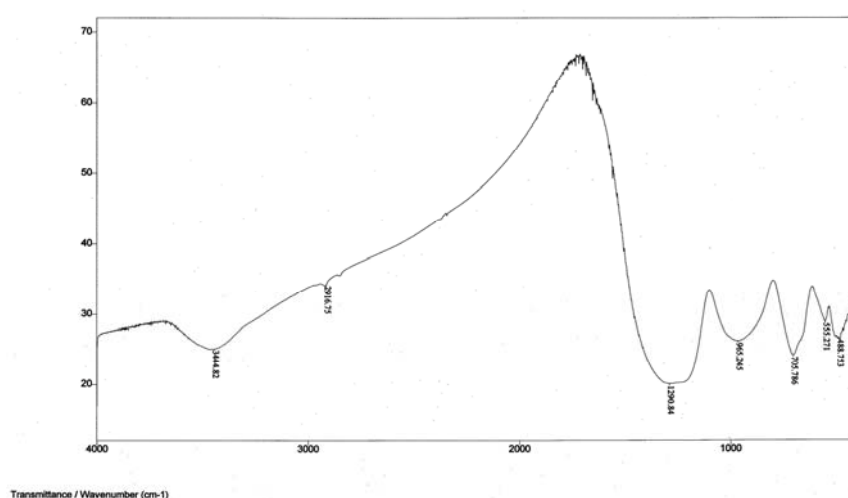


Fig. 2. IR spectrum of glass ceramics

On the basis of the IR spectrum we observe lines at 560 and at 660 cm^{-1} as well as at 1350 cm^{-1} , which indicate the presence of Cr_2O_3 . It is these lines that reveal that highly toxic chromium is bonded as an oxide with a silicate phase and that it is chemically completely inert. Apart from detoxication of chromium, glass-ceramics gets an aesthetic value because Cr_2O_3 is a very well-known pigment and it gives a very beautiful green colour. Stronger in intensity and its form, the line in the range from 600 to 800 cm^{-1} confirms the presence of silicate phase with the dominant content of aluminosilicates in the form of $\text{Al}_2\text{O}_3 \times \text{SiO}_2 \times 2\text{H}_2\text{O}$. Likewise, during melting at high temperature the elimination of crystal water in the structure due to no lines at 1630 cm^{-1} and the dominant presence of copper (II)-titanate (IV) (CuTiO_3) are obvious, based on the form and intensity of the lines in the range from 400 to 800 cm^{-1} . These lines (from 400-800 cm^{-1}) reveal the transformation of highly toxic copper and titanium, which are bonded in the form of oxides as solid solutions and are completely chemically inert, which is very important from the environmental perspective [8].

The presence of aluminosilicates in the form of $\text{Al}_2\text{O}_3 \times 2\text{SiO}_2 \times 2\text{H}_2\text{O}$ confirms the obtained glass-ceramic structure with the bonding of hazardous and harmful substances (CuTiO_3 , Cr_2O_3), which qualifies them as chemically inert.

The XRD analysis of samples prepared from a compact piece or powder was conducted with a SIEMENS D500 powder diffractometer. Recording was done with $\text{CuK}\alpha$ radiation ($\lambda = 1,54184 \text{ \AA}$) in angle ranges 5-90 $^\circ 2\theta$ at the speed of 0,02 $^\circ 2\theta/\text{s}$. Identification of crystal phases in samples was conducted by means of *Diffra^{plus}* software and PDF (Powder Diffraction File, PDF 2) database [9].

Sample diffractogram (fig. 3) indicates a presence of a significant quantity of amorphous phase, which causes a wide diffraction profile at about 28 $^\circ$ 2θ . The $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ crystal phase and substantial quantities of elemental lead were identified in the samples.

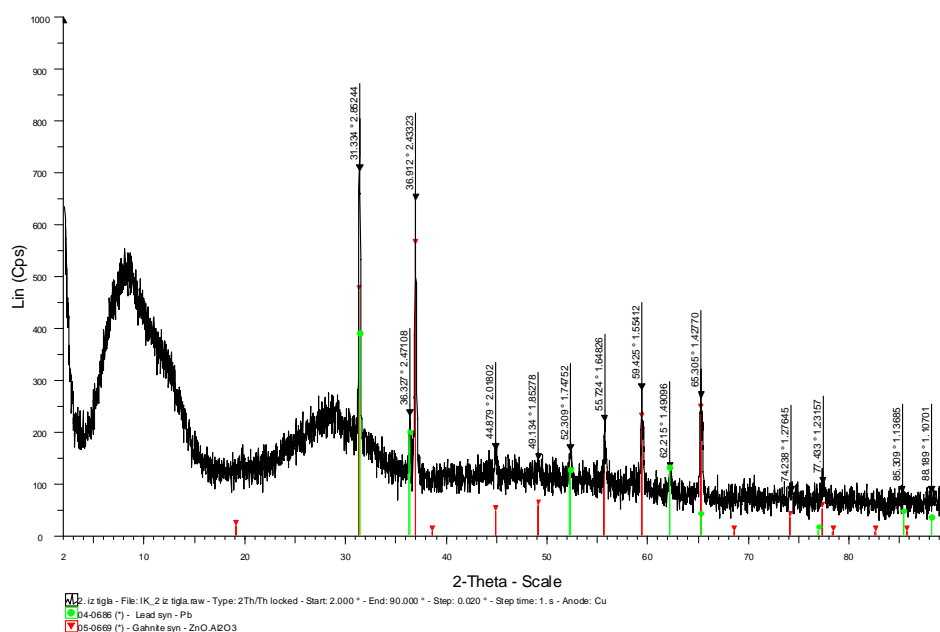


Fig. 3. XRD spectrum of glass-ceramics

Conclusion

Through application of standard procedures U.S. EPA 1997/222, designation of low- and high-flow metal fractions, we identified the ecological risk of the disposal of galvanic

sludge and aluminium slag, which are classified as hazardous waste. If they are not processed or properly disposed of, high-flow metal fraction is easily eluted with atmospheric precipitation, thus infiltrating and polluting the environment. The low-flow fraction is conditionally mobile and represents the reservoir of the high-flow fraction. Accordingly, waste galvanic sludge and aluminium slag were inactivated by sintering into a useful product – glass-ceramics. The FT-IR and XRD spectra confirmed chemical-phase transformations with the bonding of toxic metals (Zn, Pb, Cr, Cu, Cd, Ti, etc.) to the aluminosilicate phase in the form of solid solutions.

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Садржај: Методе пречишћавања галванских отпадних вода које се најчешће примењују у Републици Србији припадају типу конвенционалних система за пречишћавање (хемијска оксидација и редукција, неутрализација, коагулација, флокулација и таложење). Ове методе имају за последицу стварање отпадног муља који, уколико се адекватно не стабилизује, представља опасну материју. Такође, алуминијумска шљака, која настаје топљењем и ливењем алуминијума и његових легура, представља опасан отпад. У том смислу, у раду је, најпре, утврђен еколошки ризик галванског муља и алуминијумске шљаке, а затим је описан поступак стабилизације ових отпадних материја, превођењем у структуру стакло-керамике процесом синтеровања. Добијени производ је анализиран Фуријеовом трансформацијом инфрацрвеном спектроскопијом (FT-IR) и рендгенском дифракционом анализом (XRD). Предмет рада је еко-технолошки поступак добијања стакло керамике из галванског муља и алуминијумске шљаке. Циљ рада је инкорпорирање токсичних метала из галванског муља и алуминијумске шљаке у производ стакло-керамике, у облику чврстих раствора.

Кључне речи: галвански муљ, алуминијумска шљака, стакло керамика, еколошки ризик.